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REVIEW ARTICLE

Synthesis and characterization of gallium oxide nanoparticles

Kh.M. Al-khamis, Refaat M. Mahfouz, Abdulrahman A. Al-warthan, M. Rafiq H. Siddiqui *

Department of Chemistry, College of Science, King Saud University, P.O. Box 2455, Riyadh 11451, Saudi Arabia

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Abstract This review is based on the literature describing several methods for the synthesis of gallium oxide nanoparticles. Several techniques have been used for the synthesis of gallium oxide Ga_2O_3 nanoparticles. Gallium oxide Ga_2O_3 nanoparticles have been synthesized from different precursors. Different synthetic methods and different precursors produce nanoparticles which vary in size and shape. Over a dozen of synthetic methods for preparation of gallium oxide Ga_2O_3 nanoparticles together with the characterization techniques used have been discussed.

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* Corresponding author.
E-mail address: rafiqs@ksu.edu.sa (M. Rafiq H. Siddiqui).

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1. Introduction

Nano-sized materials possess unique electronic, optical and magnetic properties superior to traditional bulk materials due to their quantum size effects. They also serve as potential building blocks for high performance electronic and optoelectronic devices. Indeed quasi one-dimensional nanosized materials, including GaAs, GaN, GaO_2 and SiO_2 have been fabricated (Zhang et al., 1999), and they have been used in high gain field effect transistor and low threshold laser. Research into the synthesis and characterization of various forms of nanosized materials has, therefore, become a very important research topic in recent years.

As for gallium oxide, we know that monoclinic gallium oxide (β-Ga_2O_3) is chemically and thermally stable compound with a wide-band gap of 4.9 eV (Tippins, 1965). It exhibits conductive and photoluminescence properties (Binet and Gourier, 1998), therefore, it is a promising candidate for application as a transparent conducting material in next generation optoelectronic devices. Ga_2O_3 has recently attracted interest due to its applications ranging from gas sensors (Weh et al., 2001; Trinchi et al., 2004) and nano-structured materials to important materials in catalysis (Meitzner et al., 1993; Iwasa and Takezawa, 2003; Bonivaradi et al., 2000; Meriaudeau and Naccache, 1991). Gallium oxide is an important functional material. It has been used as insulating barrier for spin-dependent tunneling junctions (Li et al., 2000). Manganese-activated gallium oxide has been demonstrated as an electroluminescent phosphor (Miyata et al., 2000). Crystalline gallium oxide nanowires have been found to give a blue light emission (Wu et al., 2000). Nanosized gallium oxide with large surface area/volume ratio, may have particular conduction and optical properties.

Synthetic methods and precursors are very important in obtaining material of desired properties, specially relevant to nanoparticles. Ga_2O_3 nanoparticles have been synthesized by several methods. Different starting materials have also been used to synthesize these nanoparticles which result in nanoparticles of different shape and sizes. This review details the synthetic methods from different starting materials together with the nanoparticles obtained by these methods and also the characterization techniques used for the resulting nanoparticles of Ga_2O_3.

2. Methods of preparation

2.1. *Preparation of β-Ga_2O_3 nanoparticles*

2.1.1. *Using Ga and Ga_2O_3 as starting materials without adding a catalyst*

Ga_2O_3 nanowires were fabricated via vapor–solid process in ambient atmosphere using Ga and Ga_2O_3 as starting materials without adding catalyst by Cai et al. The formation mechanism of the nanowires was analyzed by differential scanning calorimeter and thermogravimetric analysis and found to be controlled by the vapor–solid (VS) growth mechanism. The results show that there is a relatively strong exothermic peak centered at 848 °C in the DSC curve and that the TG curve quickly goes up accordingly, indicating a strong oxidation reaction at around this temperature. The oxidation process of the Ga embedded in the Ga_2O_3 powder could be roughly divided into three stages according to the DSC/TG results. The obtained results show the first stage is from its melting point (29.8 °C) to about 40 °C; the second stage is from 40 to about 838 °C; and the third one is from 838 to 1200 °C (Wu et al., 1993; Cai et al., 2008). Ga_2O_3 nanowires were fabricated by vapor–solid process in ambient atmosphere using Ga and Ga_2O_3 as starting materials without adding any catalyst. The Ga_2O_3 nanowires were found to be about 10–80 nm in diameter and several micrometers in length. This is a simple and low cost method for the synthesis of nanowires of Ga_2O_3 (Cai et al., 2008).

2.1.2. *Thermal evaporation and deposition of Ga_2O_3*

Penner et al. prepared Ga_2O_3 thin films by thermal evaporation and deposition of Ga_2O_3 on NaCl (0 0 1) cleavage planes at varying substrate temperatures, oxygen pressures and deposition rates. The substrate temperature proved to be most crucial for the structure of the gallium oxide films, ranging from low-contrast amorphous structures at low substrate temperatures (298 K) to nanosphere at higher temperatures (580 K). The stability of the films was found to be mainly determined by the interaction of substrate temperature and deposition rate. Crystallization β-Ga_2O_3 structures were obtained after oxidative, reductive and annealing treatment at and beyond 773 K suggesting that the crystallization is mainly a thermal annealing effect.

The structure of the so prepared thin film was checked by transmission electron microscopy and the results show aporous grain structure with very small crystallites that can be detected for films deposited at 298 K. Gallium oxide films exhibited considerable structural alterations if deposited at higher substrate temperatures (Wang et al., 2004; Kim and Kim, 2004). The onset of restructuring was already obvious after raising the substrate temperature to ~430 K. At this deposition temperature, the porous structure still persists, but the grains increased considerably in size and show better contrast in the TEM images. This trend is continued after raising the substrate temperature to about 473 K. An inhomogeneous structure with irregularly arranged crystals is observed, although the grains exhibit more or less the same size as those observed after deposition at 430 K. The SAED pattern, however, remains unaffected. After deposition at 530 K.

The overall film morphology is hardly changed (Penner et al., 2008).

2.1.3. *Thermal annealing of compacted gallium nitride powder*

Growth of β-Ga_2O_3 nanostructures such as nanowire, nanobelt, nanosheet, and nanocolumn studied by Jung et al. found that Ga_2O_3 can be synthesized by the thermal annealing of compacted gallium nitride (GaN) powder in a flowing nitrogen. They suggest that Ga_2O_3 vapor might be formed by the reaction of oxygen with the gaseous Ga formed by GaN decomposition. The Ga_2O_3 vapor diffuses into voids derived by compacting GaN powder and is supersaturated there, resulting in the growth of Ga_2O_3 nanostructures via the vapor–solid (VS) mechanism through the following route (Kim et al., 2002; Dai et al., 2002):

$$2GaN_{(s)} \rightarrow 2Ga_{(g)} + N_{2(g)}$$

$$4Ga_{(g)} + 3O_{2(g)} \rightarrow 2Ga_2O_{3(g)}$$

$$Ga_2O_{3(g)} \rightarrow Ga_2O_{3(s)}$$

The synthesized products were investigated by XRD, and scanning electron microscopy. For the sample oxidized at 750 °C the peaks assigned to β-Ga_2O_3 were detected along with those assigned to unreacted GaN and became more intense with increasing reaction temperature. In the case of the sample oxidized at 900 °C for 3 h, there were no detectable peaks other than those assigned to β-Ga_2O_3, (Jung et al., 2007).

The nanowire, nanobelt, nanocolumn, and orchid-like bundles composed of both nanowires and nanosheets were formed out of the inner side of the pellet annealed at 940 °C for an hour.

2.1.4. *Sol–gel method*

Ristić et al. have focused on the application of sol–gel method in the synthesis of Ga_2O_3 using gallium isopropoxide $[Ga(OC_3H_7)_3]$ as the starting material. For comparison, the precipitation by hydrolysis of $[Ga(OC_3H_7)_3]$ and from aqueous $GaCl_3$ solution by addition of aqueous tetramethylammonium hydroxide (TMAH) were utilized to obtain Ga_2O_3 precursors. The precursors thus formed and the samples obtained upon heating these precursors at high temperatures were analyzed by XRD. Amorphous phase (dominant) and nanosized α-GaOOH particles were obtained by addition of hot water and TMAH solution to the solution of $[Ga(OC_3H_7)_3]$ dissolved in 2-propanol.

A completely amorphous precipitate was obtained by hydrolysis of $[Ga(OC_3H_7)_3]$ with pure water at room temperature, and upon heating this precipitate at 500 °C the nanosized β-Ga_2O_3 particles (size ~10–20 nm) were obtained. On the other hand, α-GaOOH particles transformed at 500 °C to α-Ga_2O_3 as a single phase. Upon heating at 900 °C, in all cases only β-Ga_2O_3 was detected. The XRD analysis showed a strong dependence of the phase composition of the samples on the experimental conditions of their preparation (Ristić et al., 2005).

Sinha et al. studied the crystallization and optical properties of finite sized β-Ga_2O_3 in sol–gel derived Ga_2O_3:SiO_2 nanocomposites. They found that gallium oxide nanoparticles embedded in silica matrix with different molar ratios were synthesized by the sol–gel method. Powdered nanocomposite samples were annealed at 400, 500, and 900 °C. The gallium oxide nano particles (2–5 nm) crystallized in the β-phase at a very low temperature (~400 °C) as against the expected temperature (> 700 °C), indicating a depression of crystallization temperature under these conditions. This may be a signature of the behavior of confined nanosized particles. The indications of only Ga–O bonds and Si–O–Si bonds in FTIR spectra and peaks of gallium, oxygen and silicon in energy dispersive X-ray analysis (EDAX) confirmed the non-existence of any impurity. Room temperature photoluminescence study of the samples shows a strong blue emission at ~460 nm (Sinha et al., 2006).

2.1.5. *Doping a premixed $H_2/O_2/Ar$ flat flame with diluted trimethyl gallium in a low-pressure reactor*

Nanosized Ga_2O_3 particles in the size range between 2 and 7 nm were synthesized in an $H_2/O_2/Ar$ premixed-flame in a low-pressure reactor doped with diluted concentrations of trimethyl gallium by Ifeacho et al. The synthesized Ga_2O_3 exhibits spherical morphology and high amorphous content, which is typical for group-IIIA metal oxides synthesized in flames. Broad reflexes observed from its XRD diffractogram indicate poor crystallinity. Thermal annealing of the as-synthesized Ga_2O_3 powder yielded crystalline β-Ga_2O_3 with a monoclinic structure (Ifeacho, 2008).

2.1.6. *Thermal evaporation of β-Ga_2O_3 in a flowing gas mixture of nitrogen and CO*

Jung, prepared β-Ga_2O_3 nanobelts by the thermal evaporation of β-Ga_2O_3 in a flowing gas mixture of nitrogen and CO. He also studied the correlation between the width of gallium oxide nanobelts and the diameter of the catalysts. The results show that the nanobelts were deposited on a Si substrate via the VLS mechanism and the wbelt value of the nanobelt was linearly correlated with the d_{cat} value of the Ga droplets. Suggesting that the width of the β-Ga_2O_3 nanobelts could be controlled by adjusting the size of the Ga droplets (Fu et al., 2003; Jung, 2006).

2.1.7. *Using nonionic triblock copolymer P123*

Haneda and other researchers have developed a new route for the synthesis of Ga_2O_3–Al_2O_3 nanorods by using nonionic triblock copolymer P123 as structure directing agents. The morphology of Ga_2O_3–Al_2O_3 nanorods was further measured with TEM. From TEM image, the nanorods with average diameter of 10 ± 1 nm and average length of 50 ± 5 nm are observed (Haneda et al., 2000; Han and Ying, 2005; Luo et al., 2006).

2.1.8. *Plasma immersion ion*

Chu et al. and Ho et al. reported the synthesis of β-Ga_2O_3 nanoribbons from GaAs by plasma immersion ion implantation (PIII) and rapid thermal (RTA). Un-doped GaAs substrate was treated with PIII of nitrogen. RTA at 950 °C for 2 min produced clusters of single crystalline β-Ga_2O_3 nanoribbons. These nanoribbons have thickness of around 30 nm and 60 nm to 2 μm. The luminescence properties of β-Ga_2O_3 was studied. Two strong peaks are seen at 418 and 439 nm. The PL peak at 439 nm suggests the formation of Ga_2O_3 single crystal. This peak comes from the recombination of bound electron–hole exciton in β-Ga_2O_3 single crystal. The other peak at 418 nm shows that the β-Ga_2O_3 nanoribbons may possess optical properties with possible applications in optoelectronic nano-devices (Chu et al., 1996; Ho et al., 2003).

2.1.9. Simple precipitation technique with calcination at elevated temperature

The synthesis, characterization of morphologically different high purity gallium oxide nanopowders and the effect of pH value on the particle sizes were studied by Rambabu et al. They found that the different morphological high purity gallium oxide nanopowders were synthesized by employing a simple precipitation technique. The phase purities of the produced powders were confirmed based on the profiles of XRD. From the X-ray pattern, the phase purity of the synthesized powders was confirmed as β-Ga_2O_3. The TG/DTA analysis show a weak endothermic peak at 410 °C indicating the elimination of adsorbed moisture while exposed to ambient atmosphere. The broad exothermic peak at 840 °C may be due to the crystallization phase transformation changes taking place in the sample (Sat and Nakamura, 1982; Pokrovski et al., 1992; Ahman et al., 1996).

From the measured SEM images, it was observed that the pH value did play a dominant role in obtaining different morphological gallium oxide powders. Gallium oxide powders were synthesized at three pH values i.e. 6, 7, 8. Gallium oxide powders synthesized at pH 6.0 were found to have quadrilateral spindle like structure. At pH value 7.0, the gallium oxide powders have an irregular morphology. Gallium oxide powders synthesized at pH value 8.0 were calcined at 600 °C and 850 °C, where they were noticed to be agglomeration of nanoparticles (Rambabu et al., 2007).

2.1.10. Arc-discharge

Park et al. have studied the structural investigation of gallium oxide (β-Ga_2O_3) nanowires. They found that the gallium oxide nanowires were synthesized by electrical arc discharge of GaN powders mixed with a small amount of Ni and Co. The crystals structure of nanowires was determined by multi-channel X-ray diffractometry (MC-XRD), FT-Raman spectroscopy and transmission electron microscopy (TEM). The analyzed results clearly show that the synthesized nanowires are monoclinic gallium oxide (Ga_2O_3). Final morphology and microstructure of β-Ga_2O_3 nanowires changed depending on the presence of the transition metals in nanowires. The β-Ga_2O_3 nanowires grown by assistance of transition metals demonstrate a smooth edge surface while containing twin defects at the center. The transition metals enhanced the step growth of nanowires (Park et al., 2000; Zhang et al., 1999).

2.1.11. Heat treating

The catalytic synthesis and photoluminescence of β-Ga_2O_3 nanowires, was studied by Zhang. He found that monoclinic gallium oxide (β-Ga_2O_3) nanowires were synthesized by heat treating a composite material of GaAs and pre-evaporate Au at 1240 °C in a dry oxygen atmosphere. The catalytic Au metal generated liquid nanoclusters that serve as reactive sites confining and directing the growth of β-Ga_2O_3 nanowires during the vapor–liquid–solid growth process. The β-Ga_2O_3 nanowires have diameters ranging from 20 to 50 nm and lengths of several micrometers. Shows X-ray diffraction (XRD) spectrum of the bulk β-Ga_2O_3 nanowires. The sharp diffraction peaks in the pattern can be indexed to a monoclinic structure (Miyata et al., 2000).

Photoluminescence measurement under excitation at 250 nm shows that the bulk β-Ga_2O_3 nanowires have a stable blue emission at 475 nm and ultraviolet emission at 330 nm, which suggests possible applications in optoelectronic nanodevices (Harwig and Kellendonk, 1978; Zhang, 2001).

2.1.12. Thermal evaporating of GaN in presence of oxygen

Dai et al. have synthesized the nanoribbons and nanosheets of Ga_2O_3 by evaporating GaN at high temperature in the presence of oxygen. The as-synthesized nanoribbons and nanosheets are pure, structurally uniform, single crystalline, and free from dislocations. The nanoribbons and nanosheets all have monoclinic β-Ga_2O_3 structure.

The flat top and bottom surfaces for both nanoribbons and nanosheets are ±(1 0 0), the side surface are ±(0 1 0) and ±(1 0 1) for nanoribbons and ±(0 1 0), ±(1 0 1) and ±(2 1 2) for nanosheets. The axis direction of nanoribbon growth is along either [0 0 1] or [0 1 0]. SEM observations reveal that the products consist of a large quantity of wire-like nanostructures with typical lengths in the range of several tens to several hundreds of micrometers. The as-synthesized sample also contains a large fraction of sheet-type structure, and size of the sheets is about 10 μm across and several tens of nanometers in thickness. The nanosheets have straight edges with sharp corners, suggesting that they terminate by faceted crystallographic planes. Chemical microanalysis using EDS showed that the nanostructures obtained are Ga_2O_3 (Dai et al., 2002).

2.1.13. Metal organic chemical vapor deposition (MOCVD) method

Kim et al. have prepared large-scaled gallium oxide nanowire arrays on sapphire substrates using a reaction of a trimethylgallium (TMGa) and oxygen (O_2) mixture. The cross-section of the gallium oxide nanowires had a circular shape with the diameter of about 40–110 nm. A typical SEM image of the deposits on the surface of the sapphire substrate, reveal that the wire-like nanostructures are slightly curved with uniform diameter along the growth direction. The lower magnification SEM image show that the nanowires have a uniform distribution over a large area. The SEM image of the side view of the nanowires, indicate that the growth direction of the nanowires is randomized and the lengths of the nanowires are in the range of several micrometers. The high-magnification SEM image of a nanowire, reveal that the cross-section of the stem of the nanowire has a circular shape with no nanoparticle at its tip (Ginly and Bright, 2000; Yamazoe, 1991; Kim et al., 2004). The XRD patterns of the gallium oxide nanowires on sapphire substrates, reveals that the nanowires are totally amorphous.

3. Conclusions

Ga_2O_3 nanowires were fabricated via vapor–solid process in ambient atmosphere using Ga and Ga_2O_3 as starting materials without adding catalyst. Ga_2O_3 thin films have been prepared by thermal evaporation and deposition of Ga_2O_3 on NaCl(0 0 1) cleavage planes at varying substrate temperatures, oxygen pressures and deposition rates. Growth of β-Ga_2O_3 nanostructures such as nanowire, nanobelt, nanosheet, and nanocolumn was observed when GaN was used as starting material.

Sol–gel method has been used in the synthesis of Ga_2O_3 using gallium isopropoxide [$Ga(OC_3H_7)_3$] as the starting material, β-Ga_2O_3 particles (size ~10–20 nm) were obtained. gallium oxide nanoparticles embedded in silica matrix with different molar ratios were also synthesized by the sol–gel method. Nanosized Ga_2O_3 particles in the size range between 2 and 7 nm were synthesized in a $H_2/O_2/Ar$ premixed-flame in a low-pressure reactor doped with diluted concentrations of trimethyl gallium. β-Ga_2O_3 nanobelts were obtained by the thermal evaporation of β-Ga_2O_3 in a flowing gas mixture of nitrogen and CO. Ga_2O_3–Al_2O_3 nanorods were also synthesized by using nonionic triblock copolymer P123 as structure directing agents. β-Ga_2O_3 nanoribbons were obtained from GaAs by plasma immersion ion implantation (PIII).

Different morphological high purity gallium oxide nanopowders were synthesized by employing a simple precipitation technique. It was observed that the pH value did play a dominant role in obtaining different morphological gallium oxide powders. Gallium oxide powder were synthesized with three pH values i.e. 6, 7, 8. At pH 6.0 gallium oxide powders were found to have quadrilateral spindle like structure. At pH value 7.0, the gallium oxide powders have an irregular morphology. Gallium oxide powders synthesized at pH value 8.0 and calcined at 600 °C and 850 °C, were noticed to be agglomerations of nanoparticles. Gallium oxide nanowires were synthesized by electrical arc discharge of GaN powders mixed with a small amount of Ni and Co. The β-Ga_2O_3 nanowires grown by assistance of transition metals demonstrate a smooth edge surface while containing twin defects at the center. The transition metals enhanced the step growth of nanowires. Monoclinic gallium oxide (β-Ga_2O_3) nanowires were synthesized by heat treating a composite material of GaAs and pre-evaporate Au at 1240 °C in a dry oxygen atmosphere. The catalytic Au metal generated liquid nanoclusters that serve as reactive sites confining and directing the growth of β-Ga_2O_3 nanowires during the vapor–liquid–solid growth process.

Synthesis of nanoribbons and nanosheets of Ga_2O_3 were obtained by evaporating GaN at high temperature in the presence of oxygen. The as-synthesized nanoribbons and nanosheets are pure, structurally uniform, single crystalline, and free from dislocations. Large-scaled gallium oxide nanowire arrays on sapphire substrates were obtained using a reaction of a trimethylgallium (TMGa) and oxygen (O_2) mixture. The cross-section of the gallium oxide nanowires had a circular shape with the diameter of about 40–110 nm.

From these results it can be concluded that different shapes of gallium oxide nanoparticles can be synthesized by several methods, but the most common shape appear to be nanowires.

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